SnO$_2$-C$_{60}$ Pyrrolidine Tris-Acid (CPTA) as the Electron Transport Layer for Highly Efficient and Stable Planar Sn-Based Perovskite Solar Cells

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1. Introduction

In the past decade, Pb-based hybrid perovskite solar cells (PSCs) have achieved an impressive (up to 24.2%) power conversion efficiency (PCE).[1,2] Despite these significant progresses, the toxicity of lead limits the large-scale application of PSCs.[3] Soon after the development of Pb-based perovskites, researchers start to replace the toxic Pb due to the environmental concerns.[4,5] Sn is an attractive alternative because Sn-based perovskite has similar optical and electronic properties comparing with Pb-based perovskite.[6] However, research in this direction is hindered by the poor stability of the Sn-based perovskite in the air.[7] One of most probable reasons is reported to be the oxidation of Sn$^{2+}$ to Sn$^{4+}$.[8] The oxidation process[9] will heavily dope the perovskites and make them behave like a metallic conductor. This in turn will cause excessive carrier recombination and sometimes even short-circuit the devices. Several strategies have been developed to protect the Sn-based perovskite, such as the adding of SnF$_2$[10] controlling the reducing atmosphere,[11] the forming of 2D/3D composite[12,13]or 3D hollow structures.[14–17] In order to achieve higher efficiency and stability, Sn-based perovskite have relied on mesoporous TiO$_2$ as the electron-selective layer.[18,19] The introduction of mesoporous TiO$_2$ makes manufacture process more complex, and the high-temperature needed for processing hampers the development of perovskite-based monolithic tandem devices and flexible wearable solar cells.[20,21] In contrast, the simplicity of the planar heterojunction indicates that a planar architecture is more technically feasible.[22] Besides, planar PSCs can be fabricated via solution processing at low temperatures (<150 °C), thus greatly reducing manufacturing costs. However, compared to the mesoporous-type PSC, its planar-type counterpart suffers from very low PCE,[23,24] probably due to the poor contact of the interfaces[25] and unsuitable charge transporting layer.[23]

Here, we tried SnO$_2$ as the electron transport layer to fabricate a n–i–p planar-architecture, but was not successful. Then we introduced a hydrophilic derivative of fullerene, namely, the C$_{60}$ pyrrolidine tris-acid (CPTA) between SnO$_2$ and the perovskite. As a result, we achieved a power conversion efficiency above 7.40% for Sn-based perovskite devices with the planar n–i–p architecture. This shows that not only mesoporous-architecture devices, but also n–i–p planar-architecture devices can be highly efficient in the Sn-based PSCs. Thanks to the CPTA layer in our planar Sn-based PSCs, we attained a $V_{oc}$ of 0.72 V, which represents the highest value ever reported for FASnI$_3$ solar cells.

2. Results and Discussion

We fabricated Sn-based PSCs with the planar n–i–p architecture (Figure 1a). A SnO$_2$ compact layer deposited on the fluorine-doped tin oxide (FTO) substrate was employed as an electron transport layer. C$_{60}$ pyrrolidine tris-acid (CPTA) was then deposited onto the SnO$_2$-covered FTO substrate. Figure 1b shows the X-ray diffraction (XRD) pattern of the [en]FASnI$_3$ films. The peaks of FTO substrate are marked with black dots. The [en]FASnI$_3$ films exhibit a shift of the Bragg reflections to
smaller $2\theta$ angles compared with the FASnI$_3$ film (Figure S1a, Supporting Information). The decrease of the $2\theta$ angles indicates the increase of unit cell volume, thus confirming the existence of {en}FASnI$_3$.\cite{15} Moreover, the proton nuclear magnetic resonance ($^1$H-NMR) Spectrum and UV–vis spectra also confirm the presence of ethylenediamine in perovskite thin films (Figure S1b,c, Supporting Information). Scanning electron microscopy (SEM) was used to characterize the morphology of the {en}FASnI$_3$ film (Figure 1c). Similar to previous reports,\cite{16} the grain size of the {en}FASnI$_3$ film is obviously smaller than the FASnI$_3$ film (Figure S2, Supporting Information). We note that the Sn-based perovskite were usually fabricated by one-step method\cite{26} and two-step method,\cite{27,28} while the antisolvent assisted one-step method was rarely adopted.\cite{29} As Sn-based perovskites might crystallize faster than Pb-based perovskite materials, it is more difficult to control crystallization by means of commonly used antisolvents.\cite{17,30} The choice of antisolvent is found to be critical for high-quality films, and films prepared with chloroform as an antisolvent show the best quality (Figure S3, Supporting Information). While the exact reason is still unknown, we propose that the unique role of chloroform might be related to the hydrogen bonding formation.\cite{31} From the cross-sectional SEM image (Figure 1d), it can be observed that the perovskite layer is ≈ 400 nm thick, and the PTAA layer is about 100 nm thick. Though it has been predicted the carrier diffusion length in Sn perovskite can be over 500 nm from ultrafast spectroscopy characterization,\cite{32} efficient planar devices with Sn-based perovskite films have not been reported. Instead, mesoporous devices have to be made so that the electron diffusion can be facilitated via the mesoporous TiO$_2$ scaffold.\cite{17,32,33} Here, the photovoltaic performance shown below for the {en}FASnI$_3$ films of 400 nm thickness represents a direct proof that the electron diffusion length can be high for Sn-based perovskites.

**Figure 2** shows the Raman spectrum of the CPTA film, which is deposited on the FTO/ SnO$_2$ substrate. The Raman peaks at ≈ 600 and 1100 cm$^{-1}$ are due to SnO$_2$ film.\cite{34} The peaks at 1459 and 1564 cm$^{-1}$ can be assigned to the vibrations of C$_{60}$ rings, which is consistent with the peak of CPTA powder (blue line). This confirms the existence of the CPTA layer on the SnO$_2$. Moreover, in order to investigate the interaction between SnO$_2$ and CPTA, X-ray photoelectron spectroscopy (XPS) is carried out (Figure 2b). The photoelectron binding energy of SnO$_2$-CPTA film at Sn 3d level is slightly higher than that of SnO$_2$ film, which indicates that there is additional negative charge around the Sn atoms. As an electron donor, CPTA coordinates with Sn atoms in SnO$_2$ to form Lewis adducts. In order to measure the thickness of CPTA functional layer, we conducted tapping-mode atomic force microscopy (AFM) to observe the steps of SnO$_2$ and SnO$_2$-CPTA. The thickness of step is about 18 nm, which is the thickness of CPTA layer (Figure S4, Supporting Information).

We then studied the photovoltaic performance of the PSCs. The solar cell used the SnO$_2$ without modification of CPTA as electron transport layer shows very low efficiency. This indicates that CPTA is very important for the construction of n–i–p Sn-based PSCs. (Figure 3a). In contrast, the solar cell with SnO$_2$-CPTA electron transport layer achieved a PCE of 6.54%. Especially, The $V_{OC}$ is up to 0.722 V (forward scan). Previously, the highest $V_{OC}$ achieved for FASnI$_3$ solar cells is 0.42 and 0.47 V for normal/mesoporous and inverted architecture, respectively. The highest $V_{OC}$ achieved for hollow FASnI$_3$ solar cells is 0.48 V. We have to mention that the highest for MASnI$_3$ is 0.88 V.\cite{5} approaching its own theoretical limit. However,
poor reproducibility is definitely noted. We believe that the leap forward from 0.48 to 0.72 V here represents a breakthrough in the field. Figure 3b shows the J–V curves under simulated AM1.5 sunlight for the champion solar cell (relative humidity = 60%, RT = 25 °C), measured under reverse and forward voltage scans. The solar cell achieved a PCE of 7.40%, with a high open circuit voltage (V_{OC}) of 0.687 V, a short-circuit current density (J_{SC}) of 16.45 mA cm\(^{-2}\), and a fill factor (FF) of 0.65 when measured under a forward scan. At the same time, the solar cell achieved a PCE of 5.03%, with an open circuit voltage (V_{OC}) of 0.525 V, a short-circuit current density (J_{SC}) of 16.45 mA cm\(^{-2}\), and a fill factor (FF) of 0.58 when measured under a reverse scan. It is worth noting that there exists significant inverted-hysteresis when the solar cell is scanned in the two directions. However, as is clearly found (also mentioned in FASnI\(_3\) solar cells of inverted architecture\([13]\) but to much less degree) the trend is inverted here. We try to study how the hysteresis and J–V performance could be affected by the scan speed (Figure S5 and Table S1, Supporting Information). However, for now, we cannot explain this phenomenon in the Sn-based PSCs for the time being, but it is very probable that the timescale difference between ionic migration and electron transport inside the device might account for the finding here.\([36,37]\) Figure 3c shows the stabilized photocurrent output of the solar cell under bias of 0.435 V. The photocurrent density is \(\approx 13.9\) mA cm\(^{-2}\), which corresponds to a power conversion efficiency of 6.0%.

Figure 3. Photovoltaic performance of the [en]FASnI\(_3\) solar cells. a) J–V scan under simulated AM1.5 sunlight for a solar cell (forward scan, relative humidity = 60%, RT = 25 °C). Black line, without CPTA; red line, with CPTA. b) J–V curves of the champion device measured using both forward and reverse scan. The V_{OC} is 0.687 and 0.525 V for forward scan and reverse scan respectively (50 mV s\(^{-1}\) scanning rate). c) Stabilized photocurrent output of the solar cell under bias of 0.435 V. The photocurrent density is \(\approx 13.9\) mA cm\(^{-2}\), which corresponds to a power conversion efficiency of 6.0%. d) The EQE curve of the solar cell, and the integrate current density is 15.7 mA cm\(^{-2}\). e) Histograms of PCEs for 48 PSCs. f) Device performance of the solar cell stored in ambient air without encapsulation for 200 min (60% humidity, T = 25 °C).
The photocurrent density can be stabilized almost 100 s, even though the measurement is under an ambient condition (relative humidity = 60%, RT = 25 °C). The $J_{SC}$ integrated from the EQE curves of the PSC is 15.7 mA cm$^{-2}$, in agreement with the $J_{SC}$ obtained from the $J$–$V$ measurement (Figure 3d). We also fabricated 48 devices in several batches to testify the reproducibility of our devices, as depicted in Figure 3e. Most of the devices had more than 6% efficiency, revealing a good reproducibility of our device fabrication. The devices fabricated by our method were highly air-stable (Figure 3f). The devices without encapsulation were stored under ambient condition (60–70% humidity, T = 25 °C), and the $J$–$V$ curves were measured every 20 min (forward scan). After 200 min, the PCE is still 80% of the initial efficiency. In the first 60 min, the PCE of the newly fabricated cell did not decrease, but slightly increased, due to the slight increase of the open circuit voltage.[12] The decrease of device efficiency is mainly caused by short circuit current density and fill factor. Figure S6 in the Supporting Information shows the stability of PSCs without encapsulation in an N$_2$-filled glove box. The un-encapsulated PSCs were still measured under ambient air condition. After we placed the device in the glove box for 100 h, the PCE kept the initial efficiency of 88%.

In order to study the effects of CPTA layer on the electron transfer, photoluminescence (PL) and time-resolved photoluminescence (TRPL) technique were employed to investigate the [en]FASnI$_3$ perovskite films grown on SnO$_2$ and SnO$_2$-CPTA. As the thickness of the CPTA layer increases, the fluorescence quenching goes to a high degree (Figure 4a). Since the crystal quality of both substrates is similar on different substrates (Figure S7, Supporting Information), the quenching indicates that SnO$_2$-CPTA is more effective for charge separation than SnO$_2$.[40] In addition, the perovskite film grown on SnO$_2$ exhibited a PL decay lifetime $\tau$ of 1.5 ns, whereas the lifetime was gradually reduced to 1.2 ns on the SnO$_2$-CPTA substrate (Figure 4b), showing a faster electron transfer process. Photoemission spectroscopy is further adopted to characterize the electronic structure of [en]FASnI$_3$ (Figure 4c). The valence band maxima (VBM) of the [en]FASnI$_3$ (10% amount of en) is determined to be $-4.8$ eV, deduced from their ionization potentials. Also, the VBM of [en]FASnI$_3$ achieved by ultraviolet photoelectron spectroscopy (UPS) is consistent with the result (Figure S8, Supporting Information). Together with the optical bandgap,[15] the CBM was calculated to be $-3.3$ eV. The valence band maxima (VBM) and conduction band minima (CBM) of each functional layer are summarized in Figure 4d.[17,39] The CBM of CPTA ($-3.9$ eV) is obviously much higher than the CBM of SnO$_2$ ($-4.5$ eV), which reduces the energy loss during the electron transfer across the SnO$_2$/[en]FASnI$_3$ interface when CPTA is present. More importantly, we note that the CBM of SnO$_2$ ($-4.5$ eV) is close to the VBM of [en]FASnI$_3$ ($-4.8$ eV). The electrons transferred to SnO$_2$ might be prone to recombine with the photogenerated holes inside perovskite layer, causing low $V_{OC}$ for the devices. In other words, SnO$_2$ layer will not be effective for hole blocking in the...
{en}FASnI3 solar cells, though it might be effective for the electron transport. We note that the VBM is positioned around ~4.8 eV for Sn-based perovskites (FASnI3, MASnI3, etc.),12,17,38 and it might be generalized that the electrons transferred to SnO2 will recombine with the holes in Sn-perovskites and thus causes low Voc. For this reason, SnO2, an electron transport layer commonly used in lead-based perovskites, is no longer suitable for tin-based perovskites. We believe that this is why there were no successful examples for preparing Sn-based PSCs on SnO2. In contrast, the energy barrier at the SnO2/CPTA interface would effectively suppress charge recombination (block the holes). Therefore, the CPTA layer introduced here is essential for the success in fabricating efficient {en}FASnI3 solar cells. We also note that although the VBM of {en}FASnI3 is slightly higher than that of the PTAA, the surface of the Sn-based perovskite films is p-doped,6,18,27 producing an Ohmic contact with the PTAA layer. We also substitute SnO2-CPTA for SnO2-PC61BM as the electron transport layer. However, the performances of the PSCs are poor (Figure S9, Supporting Information). One of the differences is that the wettability of perovskite precursor solution on the surface of PC61BM is worse than that on the surface of CPTA (Figure S10, Supporting Information). Moreover, the μ of CPTA (5.4 × 10−3 cm2 V−1 s−1) is twice as high as that of PC61BM (2.1 × 10−3 cm2 V−1 s−1).39,40

3. Conclusion

To summarize, we have successfully fabricated high-quality {en}FASnI3 films after systematic optimizing of the antisolvent assisted one-step method. SnO2, an electron transport layer commonly used in lead-based perovskite, is found to be problematic for tin-based perovskite. After introduction of CPTA-modified SnO2 film as the electron selective contact, we have achieved a power conversion efficiency of 7.40% with planar structured {en}FASnI3 solar cells of the normal n-i–p architecture. A record high Voc of 0.72 V is obtained for {en}FASnI3 solar cells. Our research clarifies the confusions on {en}FASnI3 solar cells and demonstrates the feasibility of highly-efficient Sn-based perovskite for solar cell applications. This will help to establish a robust platform to research for further optimization and elucidation of the detailed working mechanisms.

4. Experimental Section

FAI and PTAA were purchased from Xi’an Polymer Technology Co. (China). The SnO2 colloid solution (tin(IV) oxide, 15% in H2O colloidal dispersion) was purchased from Alfa Aesar. SnI2 and CPTA were purchased from Sigma-Aldrich. The chloroform was purchased from J&K Scientific Ltd. (China).

CPTA/PC61BM Solution: Different concentrations (0, 1, 5 mg mL−1) of CPTA were dissolved in 1.0 mL DMF; for PCBM solution, 5 mg PC61BM was dissolved in 1 mL chlorobenzene.

Perovskite Precursor Solution: 0.408 g of SnI2, 0.032 g enI2, and 0.172 g FAI were dissolved in a mixture of DMF (0.5 mL) and DMSO (0.3 mL). Similar to the literature,110 0.024 g SnF2 was added to relieve the detrimental effects from the presence of Sn4+.118 The solution was filtered before use through a 0.22 μm filter.

HTM Solution: 32 mg PTAA (poly[ bis(4-phenyl)(2,4,6-trimethylphenyl) amine], Mn = 15 000-50 000) and 3.6 mg 4-isopropyl-4′-methyl diphenylidionium tetrakis(pentafluorophenyl) borate (TCI) was dissolved into chlorobenzene (1.6 mL). After stirring for 30 min, the solution was filtered before use through a 0.22 μm filter.

ETM Solution: The SnO2 colloid precursor solution (tin (IV) oxide), 15 wt% in H2O colloidal dispersion) was diluted to 2.5% wt. LiCl was added to the ETM solution (0.01 mmol mL−1). The diluted solution was stirred for 30 min right before being spin coated.

FTO glass (15 Ω per square, OPV tech Co., China) was used as the transparent conductive substrate for device fabrication. The substrates (1.5 cm × 1.5 cm in dimension) were sequentially cleaned via ultrasonication in aqueous detergent solution, deionized water, and isopropanol. The solvent-cleaned substrates were then treated with oxygen plasma for 6 min. For SnO2 layer fabrication, the SnO2 precursor solution was spin-coated onto the substrate at 4000 rpm for 30 s, and then the SnO2 covered substrates were annealed at 150 °C for 30 min. After that, the substrates were transferred to a N2-filled glove box. The CPTA solution was spin-coated onto the SnO2-covered FTO substrate at 2000 rpm for 30 s, and the substrates were then annealed at 80 °C for 30 min.

The {en}FASnI3 films were then fabricated through a one-step method assisted with antisolvents. After stirring the perovskite precursor solution for 20 min, the precursor solution was spin-coated onto SnO2-covered FTO substrate at 3000 rpm for 1 min. At the late stage, 0.5 mL chloroform was poured onto the substrate. After a following heating process at 110 °C for 15 min, the precursor films transformed into the desired {en}FASnI3 films.

The perovskite solar cells were fabricated in a normal device configuration: FTO/SnO2/CPTA/{en}FASnI3/PTAA/Au. PTAA was spin coated onto {en}FASnI3 films as the hole-transport layer at 1500 rpm for 30 s and annealed at 70 °C for 5 min. Finally, 80 nm Au layer was then deposited on top of CPTA for the collection of the carriers. After PTAA was deposited, the {en}FASnI3 samples were taken out of the glove box, and quickly (~10 min) got transferred to an evaporator for Au deposition.

The photovoltaic characterization of the un-encapsulated {en}FASnI3 devices was carried out under the ambient conditions in the laboratory. A Newport Sol3A solar simulator was used as the sunlight source, and the light intensity was calibrated (100 mW cm−2) with a standard Si solar cell available from Newport. A Keithley 2400 was used to bias the solar cells and to collect the current signal. The active area of the device was 0.1 cm2, which was defined by a metal mask. The incident photon-to-current Efficiency (IPCE) spectra of the devices were collected via a GloSpex IPCE system.

A PANalytical high resolution PXRD (Cu target, line, 1.5406 Å) was used for the X-ray characterization of the perovskite films. The scanning rate was set at 4° per min and the step size was 0.02°. UV–vis absorption spectra of the planar perovskite films were characterized by an UV/Vis spectrophotometer (Hitachi U-4100). SEM images of perovskite films were characterized via a field emission scanning electron microscopy (Hitachi S4800). The thickness of CPTA layer was measured via an atomic force microscope (Bruker Dimension Icon). The steady state photoluminescence (PL) spectra of the {en}FASnI3 films were collected via a NanoLog infrared fluorescence spectrometer (NanoLog FL3-2iHR). Time resolved fluorescence of {en}FASnI3 films was collected via an UltraFast lifetime Spectrofluorometer Delta flex. A Hamamatsu 479 nm diode laser was used as the excitation source. The 1H NMR spectra of films were recorded on a Bruker-500 MHz NMR (AVANCE III). XPS was carried out using an Imaging X-ray photoelectron spectrometer (Axis Ultra). Photoemission spectroscopy measurements were carried out using a photoelectron spectrometer (AC-2). Ultraviolet photoelectron spectroscopy (UPS) spectra was measured by an imaging photoelectron spectrometer (ESCALAB250Xi, ThermoFishier Scientific Ltd), with a non-monochromated He I photon source (hν = 21.11 eV). Raman spectra were measured on a Raman microscope (Horiba-Jobin Yvon system) with a wavelength ranging from 100 to 3000 cm−1.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CPTA-modified SnO₂, FASnI₃, hybrid perovskite solar cells, planar structure

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